

## Atoms and Quantum Mechanics

*Physics isn't a religion. If it were, we'd have a much easier time raising money.*  
— Leon Lederman

### Overview

By the 1880's many physicists had become a bit complacent about their description of the natural universe, thinking that most of the basic principles had been found, and that what remained was mostly a matter of filling in the details.

There were indeed some interesting details to be considered, especially in areas that were under study by chemists. The atomic theory of chemical elements seemed more and more to fit the facts, but no one had much of an idea what kind of physical system an atom might be. Then there was the matter of characteristic line spectra: light emitted by each element consists of a discrete set of wavelengths peculiar to that element. Why only these wavelengths? Why are they different for different elements?

Maxwell's theory of electromagnetism, still new but gaining acceptance, seemed to require the existence of a mysterious substance (the aether) as the medium for the transmission of electromagnetic waves. It would be important to know in which reference frame the aether is at rest, so experiments were devised to determine the velocity of the earth through the aether. These experiments gave a puzzling result: the earth seems to be *always at rest* relative to the aether. How could this be?

Finally, there was the matter of specific heats of gases. The prevailing model, which included the equipartition of energy theorem, gave wrong answers (at room temperatures) for most of those specific heats, except for inert gases such as He.

Nevertheless, to many in the 1880's these puzzles seemed to be matters which would be understood in good time in terms of the existing framework. But things changed dramatically during the next decade, and not until fifty years later would anyone again suggest that we were really understood most of the basic principles.

New discoveries came at a rapid pace:

- 1895: X-rays discovered by Roentgen
- 1896: Radioactivity discovered by Becquerel
- 1897: Electrons discovered by Thompson

- 1900: Planck proposed “quanta” to explain spectrum of radiation from heated objects
- 1905: Einstein explained away the aether in terms of special relativity
- 1905: Einstein used Planck’s quanta (photons) to explain photoelectric effect
- 1911: Nuclei of atoms discovered by Rutherford
- 1913: First workable model of atoms by Bohr
- 1923: Compton effect showed photons behaving like both particles and waves
- 1924: DeBroglie suggested that “particles” such as electrons also behave like waves
- 1925-26: Heisenberg, Born and Schrödinger developed quantum mechanics
- 1928: Dirac developed relativistic quantum theory of electron, predicting its antiparticle (positron, found in 1932)
- 1932: Neutron discovered by Chadwick

In the nearly seventy years since then many new things have been found, but they have not altered fundamentally our understanding of the principles governing the structure of atoms and molecules.

We clearly cannot discuss here all of the above discoveries, even superficially. We will concentrate on those necessary to describe atomic structure and properties of nuclei.

### **Energy levels in atoms**

Bohr’s 1913 model was based on three things he knew about:

- Rutherford’s discovery that most of the mass of an atom, and all of its positive charge, reside in a very tiny nucleus.
- A formula, put forward in 1885 by Balmer, summarizing part of the wavelength spectrum of light emitted by a hydrogen atom.
- Planck’s formula, used by Einstein, for the energy of a photon:  $E = hf$ , where  $f$  is the frequency and  $h$  is Planck’s constant.

Rutherford had considered a “planetary” model of the atom, in which electrons circulate around the nucleus like planets around the sun, bound by the Coulomb force. The problem with this picture is that orbital motion requires a radial acceleration, and an accelerated electron will (according to classical electromagnetic theory) radiate away its energy. Estimates show that an atomic electron should lose all its kinetic energy in about  $10^{-8}$  s and spiral into the nucleus. What keeps this from happening and allows atoms to be stable systems?

Bohr didn't know the answer to that, but he did know that atoms do have at least one stable state, the one in which the total energy is the lowest possible. (This is called the "ground" state.) Starting from this fact he proposed that there may be other special states available to an atom. In the absence of emission or absorption of radiation, the atom could be stable in any one of these states. He called them **stationary states**.

As to the radiation, a clue came from the Balmer formula. Atoms do not radiate with a continuous range of frequencies (as classical theory would predict for the radiation emitted while an orbiting electron loses its energy) but only with a discrete set of characteristic frequencies. The Balmer formula for hydrogen gives those frequencies that lie in and near the visible spectrum:

$$\text{Balmer formula: } f = f_0 \left( \frac{1}{4} - \frac{1}{n^2} \right), \text{ where } n = 3, 4, 5, \dots$$

Here  $f_0$  is a constant (roughly  $3.3 \times 10^{15}$  Hz). The highest frequency predicted by this formula is obtained by letting  $n \rightarrow \infty$ ; the corresponding wavelength is  $\lambda_{\min} \approx 365$  nm. The lowest frequency ( $n = 3$ ) corresponds to wavelength  $\lambda_{\max} \approx 656$  nm. All other wavelengths given by this formula lie between these limits. By 1913 many of these wavelengths had in fact been observed in the spectroscopic study of hydrogen. It was also observed that there are no wavelengths in the visible part of the hydrogen spectrum except those given by Balmer's formula.

Bohr's revolutionary assumptions were these:

- Atoms have a discrete set of stationary bound states in which they can exist. In each of these states the energy of the atom has a certain specific value, and only these energy values are allowed for the bound atom.
- In emission or absorption of radiation, the atom changes quickly from one of these states to another, a process called a "quantum jump". The ground state is completely stable because there is no state of lower energy.
- The energy difference  $\Delta E$  between the initial and final states in such a transition determines the frequency  $f$  of the photon emitted or absorbed, according to Planck's formula, i.e.,  $\Delta E = hf$ . Energy is conserved in the process.

It remained to give a formula for the energy values (called "energy levels") of the stationary states. From the Balmer formula, Bohr was able to guess that this formula has the following form:

Bohr energy level formula	$E_n = -\frac{hf_0}{n^2}$ , where $n = 1, 2, \dots$ and $f_0 = 13.6$ eV
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The negative sign for the energy is characteristic of the total energy (kinetic plus potential) of any *bound* system held together by an *attractive* conservative force for which the potential energy is taken to be zero at infinite distances. In this case it is the Coulomb force between proton and electron.

The lowest energy (ground state) corresponds to  $n = 1$ . As  $n \rightarrow \infty$  the energy rises to zero and the atom becomes unbound ("ionized"). If Bohr's model has validity the energy required to ionize the atom should be  $hf_0$ , which is about 13.6 eV. This prediction is in good agreement with experiment.

In atomic physics one gives energies in "electron volts" (eV), where 1 eV is the energy gained by an electron when it passes through 1 V potential difference, about  $1.6 \times 10^{-19}$  J.

### Line spectra of hydrogen

The frequency of a photon emitted when the atom goes from a state with  $n = n_1$  to one with  $n = n_2$  will be, according to Bohr's assumptions:

$$f_{1 \rightarrow 2} = \frac{E_{n_2} - E_{n_1}}{h} = f_0 \left( \frac{1}{n_2^2} - \frac{1}{n_1^2} \right).$$

The Balmer formula is a special case of this, in which  $n_2 = 2$ . For other values of  $n_2$  one gets other sets of spectral lines (none of which are in the visible region) all of which have been found in subsequent spectroscopic study. In this respect the Bohr model gives a complete account of the hydrogen spectrum.

### Completion of the Bohr model

Up to this point, the value of  $f_0$  had to be taken from experiment. Bohr wanted to account for it from "first principles". That is, he wanted to derive a formula for it in terms of the fundamental constants of nature such as the charge and mass of the electron, Planck's constant, the speed of light, and the constant  $k$  in Coulomb's law.

By a lucky coincidence, one can accomplish this by partial application of classical physics. Bohr gave several different arguments of this type, each of which arrives at the same result, which gave him confidence that he was on the right track.

An argument often given in textbooks involves the hypothesis that the angular momentum of the electron in an orbit is restricted to "quantized" values given by

$$L = nh / 2\pi, \text{ where } n = 1, 2, 3, \dots$$

This assumption indeed leads to the desired formula, but it is certainly not justified on classical or other grounds, being more like a shot in the dark. It is also wrong. It predicts

that the electron in the ground state ( $n = 1$ ) of hydrogen will have angular momentum  $h / 2\pi$ ; we now know that the angular momentum in that state is zero.

The quantity  $h / 2\pi$  occurs often in quantum theory and is given the special symbol,  $\hbar$ , called “h-bar”.

The idea that angular momentum is quantized is indeed correct. But the rule is not the one given above. Instead, the correct formula is

$$L^2 = \ell(\ell+1)\hbar^2, \text{ where } \ell = 0, 1, 2, \dots, n-1.$$

Justification of this formula had to wait until a full-blown quantum theory was developed in 1925-26.

Actually Bohr gave one good argument for the derivation of  $f_0$ , and in the process put forward an important idea, which he called the Correspondence Principle. This says:

**Classical physics is an approximation, which quantum physics approaches when the systems being considered are large enough to be of “classical” size.**

For the atom, this means as  $n$  becomes very large. To apply the principle, Bohr considered the frequency of a photon emitted when the atom jumps from the  $n$ th state to the  $(n-1)$ th state, where  $n$  is a large number. He argued that the frequency of this photon, as predicted by quantum theory, ought to coincide with the classically predicted frequency, which is the rotation frequency of the electron in its orbit. By requiring this agreement in the limit of large  $n$ , one arrives at the desired formula:

$$hf_0 = \frac{2\pi^2 k_e^2 e^4 m}{h^2}.$$

Substituting the values of the constants, one finds that  $hf_0$  is 13.6 eV, as desired.

The Bohr model was a great step forward in our understanding of atoms, although it left many unanswered questions and problems, among which are these:

- No explanation was given as to why an electron in a stationary state does not radiate classically on account of its radial acceleration.
- The value of the angular momentum of the ground state is wrong.
- The model does not deal successfully with atoms having more than one electron.
- The model has no power to account for binding of atoms in molecules, or for the frequency spectrum of the photons emitted by molecules.

Nevertheless, several important things in Bohr’s model have survived and are central ideas in quantum theory:

- The idea of a discrete set of stationary states as the only allowed states with definite energy. This is often called “quantization” of energy.

- The idea of the “quantum jump” transition, in which systems change quickly from one stationary state to another without passing through intermediate values of the energy.
- The formula  $\Delta E = hf$  for the frequency of radiation emitted in a quantum jump.
- The idea of quantization of angular momentum.
- The Correspondence Principle.

### Is the photon a particle or a wave? Yes, and so is the electron.

The **photoelectric effect**, in which light falling on the surface of a metal liberates electrons from the metal, was discovered as early as 1887, but the explanation of its peculiar aspects was first given in 1905 by Einstein. In his explanation, the incident light is treated as “hailstorm” of particles (photons), each having energy  $E = hf$ , each of which can give this energy (or less, but not more) to a particular electron in the metal. In this picture the release of each electron from the metal surface is an individual event, caused by absorption of one photon from the incoming light.

If the minimum energy necessary to free the electron from the metal surface is denoted by  $\phi$  (this is called the “work function” and is a property of the material) then the maximum possible kinetic energy of the electron is given by conservation of energy:

Photoelectric effect: Einstein theory

$$K_{\max} = hf - \phi$$

Since kinetic energy cannot be negative, this shows that there is a *threshold frequency*,  $f_{\min} = \phi / h$ , below which no electrons will be released, no matter how intense the light may be. If the frequency is above the threshold, then the number of released electrons is proportional to the intensity (which is equal to the energy of each photon times the number of photons striking unit area in unit time).

In this phenomenon light — known from many experiments in the previous century to exhibit wave behavior — seems to concentrate its energy in discrete packages, much like particles. This “dual” character of light was quite puzzling to physicists of the time.

The **Compton effect** (discovered in 1923) is a change in the frequency of X-rays when they are scattered from free electrons. (Classical physics predicts *no* change in the frequency of the scattered radiation.) Compton explained the phenomenon by treating it as an elastic collision between two particles, the electron and the X-ray photon. The photon gives part of its energy to the electron in the collision, and consequently emerges with a lower frequency than before. The success of this theory gave more support to the idea that the photon has particle aspects (localized energy and momentum) as well as wave aspects (frequency and wavelength).

A year later DeBroglie argued on theoretical grounds that all matter must have this dual character. In particular, he suggested that an electron with momentum  $p$  should be characterized by a wavelength given by the same formula obeyed by photons:

DeBroglie wavelength	$\lambda = h / p$
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In 1927 this conjecture was verified when electrons scattered from a crystal showed the same diffraction pattern as X-rays of the corresponding wavelength. Over the years the wave properties of “particles” have been used in many ways, including the study of crystal structure using neutrons of the appropriate wavelengths.

How can something be both a particle and a wave? In the everyday world described by classical physics those properties are mutually exclusive. But at the subatomic level — for which we have no direct experience from our senses — things are simply different. All the objects we observe in the everyday world are very large compared to electrons or atoms, and the “classical approximation” appears to us to be the way things behave. But in reality everything obeys the laws of quantum mechanics — although we are not through our senses aware of it. This may give us conceptual difficulties, but we must set those aside and trust the experimental facts. In particular, we must not expect the microscopic world to be subject to visualization in our ordinary terms. We sometimes sketch “pictures” of atoms, but we must be careful not to take them literally.

## Quantum mechanics

Since Newton’s laws and other principles of classical physics fail at the subatomic level, it was necessary to seek (to a great extent by guessing) the correct laws and principles. Many of these were found in the years between 1925 and 1935, beginning with a theory of quantum mechanics proposed by Heisenberg in 1925.

An alternate version of the theory put forward by Schrödinger in 1926 resulted from a search for a new wave equation to describe the “matter waves” proposed by DeBroglie. This led to the famous Schrödinger equation, solutions of which allow determination of many things, such as the energy level structure of atoms and the “transition rates” for quantum jumps. Schrödinger was able to show that his version of quantum mechanics and Heisenberg’s are mathematically equivalent; Schrödinger’s is generally regarded as easier to use.

The solutions of the Schrödinger equation (wave-functions) are usually denoted by  $\psi$  (Greek “psi”). From the beginning there was much argument over the physical meaning of  $\psi$ . It describes a wave of some sort, but what is it that is “waving”? It cannot be an observable physical quantity, because  $\psi$  is not in general a real-valued function.

That is, a particular numerical value of  $\psi$  is a complex number, with both a real and an imaginary part. No observable quantity can be complex.

After over a year of discussion and argument — and over the strong objections of both Einstein and Schrödinger himself — a consistent interpretation was arrived at, largely by Bohr, Born and Heisenberg. In their so-called “Copenhagen doctrine” of 1927 the wave-function  $\psi$  plays a very indirect role, determining the *probabilities* of various possible outcomes of measurements, but not predicting exactly what any single measurement will give. Since one generally does measurements at the microscopic level on large numbers of presumably identical systems, the data are always statistical, and quantum theory successfully predicts the distributions shown in the data. The set of predicted probabilities evolves in time in a way completely determined by the Schrödinger equation, so in that sense the theory is “deterministic.” But that the theory predicts *only* probabilities was regarded by many as a flaw — it still is by some. It may be (as the true believers assert) that no theory could ever do any better. In any case, quantum mechanics including the Copenhagen doctrine has met successfully all its tests for over 80 years, and has explained many puzzling and counter-intuitive aspects of the physical world at the microscopic level. It is the best we have until now.

### The uncertainty principle.

The wave-particle duality of all matter is built into quantum mechanics. One interesting aspect of this is the so-called Uncertainty Principle, discovered by Heisenberg.

If an entity has wave properties, it cannot be “localized” completely, i.e., it cannot be located entirely at a single point. The best one can do is to create a short pulse, or “wave packet”, with a small spatial “spread” which we will call  $\Delta x$ .

Formation of such a wave packet is done by superposing harmonic waves having various wavelengths and phases. We will call  $\Delta k$  the “spread” of different values of  $k = 2\pi / \lambda$  needed to make up the packet.

In precise terms,  $\Delta x$  and  $\Delta k$  are the standard deviations of the distributions of the variables  $x$  and  $k$ .

A general theorem, valid for any wave theory, relates these “spreads”:

$$\Delta x \Delta k \geq \frac{1}{2}.$$

Now DeBroglie’s formula can be written as  $p = h / \lambda = \hbar k$ . A spread in  $k$  thus implies a spread in  $p$ . The general theorem then says that

$$\Delta x \cdot \Delta p \geq \frac{1}{2} \hbar .$$

Using the Copenhagen doctrine, Heisenberg argued that  $\Delta x$  and  $\Delta p$  should be interpreted statistically as standard deviations of the results of a set of identical measurements (at the same time) of the position ( $x$ ) and the momentum ( $p$ ) of the “particle” under study. The inequality is then interpreted as follows:

### Heisenberg uncertainty principle

It is impossible to determine both  $x$  and  $p$  simultaneously with infinite precision; the product of the uncertainties in these quantities obeys  $\Delta x \Delta p \geq \frac{1}{2} \hbar$ .

Here  $p$  stands for the  $x$ -component of the momentum. A similar relation holds for the  $y$  and  $z$  components.

There are many strange things at the microscopic level that this principle helps us to understand. Consider as an example a particle that can slide back and forth on a frictionless wire, between two rigid walls separated by distance  $L$ . What is its lowest possible kinetic energy?

In classical physics we would answer simply that its lowest kinetic energy is zero, since the particle can be at rest. But a particle at rest has momentum *precisely* zero, and therefore has  $\Delta p = 0$ . By the uncertainty principle,  $\Delta x$  must then be infinite, i.e., we must have no idea where the particle is. But we *know* it to be between the walls, so  $\Delta x$  can be no larger than  $L$ . Therefore  $\Delta p$  cannot be zero, and *the particle cannot be exactly at rest*. Its lowest possible kinetic energy is *not* zero.

In fact one can solve the Schrödinger equation for this situation rather easily, and the lowest allowed kinetic energy is indeed proportional to  $1/L^2$ . The particle can be at rest only if  $L$  is infinite, i.e., if the particle has equal probability of being *anywhere*.

This case illustrates a general rule:

**A particle confined to a restricted region of space cannot be exactly at rest.**

The minimum average energy that such a system must have is called its “zero point” energy.

The restrictions of the uncertainty principle are of no importance in our everyday life, because  $\hbar$  is negligibly small in that situation. But it does show that Newton’s 2<sup>nd</sup> law could not possibly be used to determine particle motions at the microscopic level. For to predict a particle’s trajectory using that law we must know *with precision* the initial position and momentum of the particle, which is just what the uncertainty principle forbids. Indeed, it shows that there is no such thing as a trajectory at the microscopic level. One cannot (even in principle) follow an electron in its motion within an atom; one can only discuss the probabilities of it being found in various places.